

XXV. *On the Variation of the Temperature of boiling Water.* By Sir George Shuckburgh, Baronet, F. R. and A. S. and Member of the Academy of Sciences and Belles Lettres at Lyon.

Read March 11, 1779.

THE heat of boiling water having for some years been used as one of the terms for graduating the scale of thermometers; together with the particular attention the Society has lately given (*vide* the Report of the Committee, Phil. Transf. vol. LXVII.) to this branch of inquiry, and I may add the singular success with which this age and nation has introduced a mathematical precision, hitherto unheard of, into the construction of philosophical instruments, will render it unnecessary for me to say more in respect of the following experiments, than simply to lay them before the Royal Society.

That the heat of boiling water was variable, according to the pressure of the atmosphere, seems to have been known to FAHRENHEIT as early as the year 1724<sup>(a)</sup>.

(a) *Vide* Phil. Transf. N° 385. wherein is proposed a curious project of determining the weight of the atmosphere by means of a thermometer alone, under the title of “Barometri novi descriptio.”

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A few years after this, Messieurs LE MONNIER and CASSINI (*Mem. de l'Acad. des Sc. pour 1740*) made some decisive observations, to shew that this quantity was very considerable. It was left, however, for Mr. DE LUC to make a much more compleat series of experiments, which he has described and reduced into system in his *Recherches sur la Variation de la Chaleur de l'Eau bouillante*. It remained only that these should be verified. Towards the latter end of the year 1775 I had an opportunity of repeating these observations with a small pocket thermometer of about six inches long, made by Mr. NAIRNE; an instrument, it must be confessed, not very accurate for such an examination, but with which I thought, however, I could observe to within a quarter of a degree; my object at that time, amidst a variety of other philosophical pursuits, being to assure myself that the variation took place, rather than critically to examine the quantity of it. I shall relate these observations, as the result of them upon my return to England led me to some more accurate.

Table of observations of the boiling-point, made in a journey over the Alps.

| Place of observation. | Height of the barometer. | Heat of boiling water by observat. | Heat of boiling water by Mr. DE LUC's thermometer | Diff. | Difference in $\frac{1}{100}$ of total. |
|-----------------------|--------------------------|------------------------------------|---------------------------------------------------|-------|-----------------------------------------|
|                       | Inches.                  | °                                  | °                                                 | °     |                                         |
| Bologna,              | 30.21                    | 213.5                              | 213.5                                             | -0,0  | 0                                       |
| Geneva,               | 28.60                    | 210.4                              | 210.9                                             | -0,5  | -16                                     |
| Modane,               | 26.61                    | 207.3                              | 207.4                                             | -0,1  | -2                                      |
| Lannebourg,           | 25.75                    | 205.1                              | 205.9                                             | -0,8  | -9                                      |
| Mount Cenis,          | 24.03                    | 201.2                              | 202.6                                             | -1,4  | -11                                     |
| Ditto,                | 23.91                    | 201.1                              | 202.4                                             | -1,3  | -10                                     |
|                       |                          |                                    |                                                   | Mean  | $\frac{9}{100} = \frac{1}{11}$          |

The second column gives the height of the barometer at the time of observation; the fourth, the heat of boiling water deduced from Mr. DE LUC's rules, compared with the lowermost observation, or that under the greatest pressure; the sixth gives the difference between the theory and the experiment in the motion of the boiling point in hundredth parts of the whole space described: from whence it might be concluded, that the motion or variation of the boiling point with a given variation in the pressure of the atmosphere was  $\frac{9}{100}$  or  $\frac{1}{11}$  greater

greater than by the theory alluded to <sup>(b)</sup>. But these were but gross experiments, and perhaps unworthy of such a competition. They induced me, however, to make the following. In the beginning of last year (1778) with the assistance of Mr. RAMSDEN, I procured a most excellent thermometer, every way adapted for this purpose. It was about fourteen inches long, but the interval between freezing and boiling only  $8\frac{1}{4}$  inches <sup>(c)</sup>, and though every degree was something less than the  $\frac{1}{10}$ th of an inch, yet, by means of a semi-transparent piece of ivory, which applied itself close behind the glass tube, sliding up and down in a groove cut in the brass scale for that purpose, carrying a hair-line division, at the extremity of which was a vernier dividing each de-

(b) The same instrument immersed in snow just melting at the top of Mount Cenis fell to  $32^{\circ}$ , the point of freezing observed at the level of the sea.

(c) It may possibly be suggested, that if this interval had been greater, *viz.* 20, 30, or 40 inches, I should have had a much larger scale and more convenient instrument; but in this, as in most other mechanical contrivances, our progress beyond certain limits is prevented; for if the perpendicular height of the column of quicksilver be much increased, the weight of it will be such as to distend the ball, and the instrument may differ from itself in a vertical and horizontal position by half a degree, as I have seen in a tube only fifteen inches long; and if this circumstance be endeavoured to be corrected by making the bulb of the thermometer thicker, its sensibility will be proportionably diminished. If my experience were to lead me to conclude any thing, I should consider a tube of a foot long as a *maximum*, and the bore of such a diameter as to admit a ball of a quarter or one fifth of an inch.

gree into ten; with, moreover, a lens of an inch focus; this apparatus being made moveable first by the hand, and more delicately by means of a micrometer screw; whose head was divided into twenty-five divisions, each equal to the fortieth of a degree (for so truly cylindrical was the tube, which had been with care expressly selected from a great quantity of glass, that the divisions in the neighbourhood of the freezing point did not differ from those near the boiling point by so much as  $\frac{1}{40}$ th of a degree, and this variation appeared in other parts of the tube strictly uniform, as was found by breaking the column of mercury); by means I say of this apparatus I was enabled to read off any height of the thermometer to within  $\frac{1}{50}$ th of a degree. The vessel, in which the water was boiled, which was always spring water, was a cylindrical tin pot, 13 inches high and  $4\frac{1}{4}$  inches wide, with a top something resembling that described in Mr. DE LUC's work, contrived to carry off the steam without incommoding the observer, with a waste pipe for the superfluous water in boiling, which might otherwise fall upon the fire and extinguish it. The ball of the thermometer was immersed to within  $2\frac{1}{2}$  inches of the bottom of the vessel, and  $10\frac{1}{2}$  inches below the surface of the water, so that as near as might be the whole column of mercury was exposed to the heat of boiling water,

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there being only  $15^{\circ}$  or  $20^{\circ}$  of the scale, equal about  $\frac{1}{50.0}$  part rising out of the water exposed to the temperature of the steam, which in one or two experiments was found to be  $180^{\circ}$  or  $190^{\circ}$ , so that the correction for this defect of heat would only amount to a very few hundredths of a degree, perhaps about ,04 or 05, which, as the instrument was exposed to the same circumstances as near as might be in all the observations, I have taken no notice of. I thought it necessary to say thus much respecting the precision of the instrument and the apparatus, and shall now relate the observations at length.

Table of the observations.

| °Z | Place of observation.                                 | Height of the barometer. | Therm. at 50°. | Barometer reduced to the heat of 50°. | Boiling point.                                            | Mean boiling point. |
|----|-------------------------------------------------------|--------------------------|----------------|---------------------------------------|-----------------------------------------------------------|---------------------|
|    |                                                       | Inch.                    | °              | Inch.                                 | ° 40ths.                                                  | ° 100ths            |
| 1  | Summit of Snowdon in Carnarvonshire, Aug. 15, 1778, } | 26,487                   | 46             | 26,498                                | 207, 8<br>206,38                                          | 207,07              |
| 2  | Top of Carn Cwm Gafr, Aug. 16, 1778, }                | 27,274                   | 62             | 27,241                                | 208,27<br>208,24<br>208,28<br>208,19<br>208,29            |                     |
| 3  | In the descent from ditto,                            | 27,957                   | 51             | 27,954                                | 209,28½<br>209,37<br>209,39<br>209,32<br>209,32<br>209,40 | 209,87              |

Table of observations continued.

| Number. | Place of Observations.                         | Height of the barometer. |    | Barometer reduced to the heat of 50°. | Boiling point.                                                     | Mean boiling point. |
|---------|------------------------------------------------|--------------------------|----|---------------------------------------|--------------------------------------------------------------------|---------------------|
|         |                                                | Inch.                    | °  | Inch.                                 | ° 40ths.                                                           | ° 100ths            |
| 4       | Shuckburgh, Dec. 3, 1778,                      | 28,360                   | 44 | 28,377                                | 210,17½<br>210,20½<br>210,20½<br>210,21½                           | 210,50              |
| 5       | Ditto, Oct. 23, 1778,                          | 28,690                   | 47 | 28,699                                | 211, 8<br>211,10<br>211,11<br>211,13<br>211,12<br>211,10           | 211,27              |
| 6       | Ditto, Sept. 27, 1778,                         | 28,910                   | 54 | 28,898                                | 211,19½<br>211,20½<br>211,24½<br>211,17½<br>211,14½                | 211,50              |
| 7       | Ditto, Nov. 7, 1778,                           | 28,990                   | 47 | 28,999                                | 211,23<br>211,24<br>211,25<br>211,23                               | 211,60              |
| 8       | Llanberis, Carnarvonshire, }<br>Aug. 13, 1778, | 29,477                   | 60 | 29,447                                | 212,22                                                             | 212,55              |
| 9       | London, Jan. 27, 1779,                         | 29,790                   | 45 | 29,805                                | 212,35<br>212,40<br>212,42<br>212,36<br>212,36<br>212,38<br>212,39 | 212,95              |

Table

Table of Observations continued.

| Number. | Place of observation.  | Height of the barometer. | Thermometer reduced to the heat of 50° | Boiling point.                                                                                                  | Mean boiling point. |
|---------|------------------------|--------------------------|----------------------------------------|-----------------------------------------------------------------------------------------------------------------|---------------------|
|         |                        | Inch.                    | Inch.                                  | ° 40ths.                                                                                                        | ° 100ths            |
| 10      | London, Jan. 28, 1779, | 29,990                   | 44 30,008                              | 213, 5<br>213, 8<br>213, 10<br>213, 9<br>213, 18<br>213, 10<br>213, 6<br>213, 6<br>213, 11<br>213, 12<br>213, 8 | 213,22              |
| 11      | Ditto, June 10, 1778,  | 30,250                   | 64 30,207                              | 213,20<br>213,23<br>213,24<br>213,26<br>213,23½                                                                 | 213,58              |
| 12      | Ditto, Dec. 27, 1778,  | 30,468                   | 43 30,489                              | 214, 5<br>214, 9<br>214, 6<br>214, 2<br>214, 5<br>214, 7<br>214, 7<br>214, 5                                    | 214,15              |
| 13      | Ditto, Dec. 24, 1778,  | 30,750                   | 46 30,763                              | 214, 18<br>214, 12<br>214, 15                                                                                   | 214,37              |

Table

Table of observations continued.

| Number. | Place of observation.                                                               | Height of the barometer. | Therm. at 50°. | Barometer reduced to the heat of 50°. | Boiling point.                                                                                    | Mean boiling point. |
|---------|-------------------------------------------------------------------------------------|--------------------------|----------------|---------------------------------------|---------------------------------------------------------------------------------------------------|---------------------|
|         |                                                                                     | Inch.                    | °              | Inch.                                 | ° 40ths.                                                                                          | ° 100ths            |
| 14      | London, Dec. 25, 1778,                                                              | 30,838                   | 47             | 30,847                                | 214,35<br>214,32<br>214,33<br>214,34<br>214,35<br>214,31<br>214,33                                | 214,83              |
| 15      | Ditto, at the Adelphi Wharf, $3\frac{1}{2}$ feet above high water, Dec. 26, 1778, } | 30,948(d)                | 47             | 30,957                                | 214,35<br>214,39<br>214,40<br>214,38½<br>214,41<br>214,37<br>214,41<br>214,40<br>214,40<br>214,34 | 214,15              |

The numbers in the fifth column are the corrected heights of the barometer reduced to one and the same temperature, *viz.* 50°, which was necessary in order to have the true proportion of the pressure of the atmosphere, whose influence seems to have so considerable a

(d) This is the greatest height of the barometer that I have ever known, and, as far as I have been able to collect the highest point, that it has ever been seen to stand at in any country where observations have been made and recorded, since the first invention of this ingenious instrument.

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share in the heat of boiling water. Column the sixth shews the height the thermometer stood at in water boiling very fast in degrees and 40ths of a degree; where it will be seen, that the observation was repeated, as the heat is given of every separate trial, which is, perhaps, the best criterion of the confidence that is to be placed in the mean result, shewn in column the seventh expressed in hundredths of a degree.

Having collected this series of experiments, I was anxious to see how far they corresponded with Mr. DE LUC's, and upon comparison of N° 1. and N° 15. I found that the decrease of the boiling heat was  $\frac{.47}{100}$  greater than the rules admitted of from an alteration of the pressure of the atmosphere of  $4\frac{1}{2}$  inches. This difference led me into an examination of all my observations, to see how far they were consistent with themselves; how far they disagreed from Mr. DE LUC's; and, lastly, what general conclusion might be drawn from them.

To avoid in some measure, or at least correct, the errors of observation, the mean of N° 1. and N° 2. the mean of N° 6. and N° 7. and of N° 14. and N° 15. was taken instead of either observation separately; the first and third of these means as two extreme terms, and the second as an intermediate one: with these it was very easy by interpolation or proportion to deduce any other

intermediate term, and consequently from the mean of six to examine all the fifteen observations. Thus, on a comparison of N° 1. and 2. with N° 14. and 15. the mean motion of the boiling point in that interval for one inch of the barometer (*viz.* when the mercury stands at 28,886 inches) is =  $1^{\circ},743$ ; according to Mr. DE LUC this is  $1^{\circ},65$ . By a similar comparison of N° 1. and 2. with N° 6. and 7. the mean motion of the boiling point in that interval (*viz.* at 27,908 inches) for one inch is =  $1^{\circ},779$ ; by Mr. DE LUC =  $1^{\circ},73$ . And, lastly, comparing the mean of N° 6. and 7. with the mean of N° 14. and 15. the mean motion of the boiling point in this interval (*viz.* at 29,925 inches) for one inch is =  $1^{\circ},709$ ; by Mr. DE LUC =  $1^{\circ},59$ . It should follow then, that, within the limits of my experiments, the alteration or motion of the boiling point is greater <sup>(e)</sup> by  $\frac{1}{18}$  than from that gentleman's observations, that the heat of boiling water is not directly in the simple ratio of the height of the barometer, nor yet is the progression so rapid as Mr. DE LUC observed it. It may be somewhat satisfactory to see the observations collated and compared.

(e) It is true, that my observations in Savoy give this difference  $+\frac{1}{18}$  those of Mr. LE MONNIER equal  $+\frac{1}{18}$  (Vide *Recherches sur l'At.* § 964.); and though, perhaps, neither the one nor the other are intirely unexceptionable, they tend, however, something to confirm, although alone they may be unable wholly to support, such a supposition.

| N <sup>o</sup> | Height of the barometer. | Boiling point by observation. | Boiling pt. by Mr. DE LUC's rules. | Error. | Boiling point by interpolation from N <sup>os</sup> 1, 2, 6, 7, 14, and 15. | Error. |
|----------------|--------------------------|-------------------------------|------------------------------------|--------|-----------------------------------------------------------------------------|--------|
|                | Inch.                    | °                             | °                                  | °      | °                                                                           | °      |
| 1              | 26,498                   | 207,07                        | 208,54                             | +0,47  | 207,18                                                                      | +0,11  |
| 2              | 27,241                   | 208,64                        | 208,84                             | +0,20  | 208,52                                                                      | -0,12  |
| 3              | 27,954                   | 209,87                        | 210,03                             | +0,16  | 209,80                                                                      | -0, 7  |
| 4              | 28,377                   | 210,50                        | 210,81                             | +0,31  | 210,56                                                                      | +0, 6  |
| 5              | 28,699                   | 211,27                        | 211,34                             | +0, 7  | 211,11                                                                      | -0,16  |
| 6              | 28,898                   | 211,50                        | 211,67                             | +0,17  | 211,47                                                                      | -0, 3  |
| 7              | 28,999                   | 211,60                        | 211,85                             | +0,25  | 211,64                                                                      | +0, 4  |
| 8              | 29,447                   | 212,55                        | 212,74                             | +0,19  | 212,42                                                                      | -0,13  |
| 9              | 29,805                   | 212,95                        | 213,15                             | +0,20  | 213,03                                                                      | +0, 8  |
| 10             | 30,008                   | 213,22                        | 213,47                             | +0,25  | 213,49                                                                      | +0,27  |
| 11             | 30,207                   | 213,58                        | 213,79                             | +0,21  | 213,71                                                                      | +0,13  |
| 12             | 30,489                   | 214,15                        | 214,23                             | +0, 8  | 214,19                                                                      | +0, 4  |
| 13             | 30,763                   | 214,37                        | 214,66                             | +0,29  | 214,65                                                                      | +0,28  |
| 14             | 30,847                   | 214,83                        | 214,79                             | -0, 4  | 214,79                                                                      | -0, 4  |
| 15             | 30,957                   | 214,96                        | 214,96                             | ,0     | 214,96                                                                      | ,0     |

I shall make no deductions from this comparison, but leave them to the leisure of the reader. It will, however, probably be inquired, how the thermometer came to stand at 213° in boiling water, when the barometer was about 30 inches, 212° being the degree by which that heat is expressed on FAHRENHEIT's scale? The answer is easy: it was an error in the making of the instrument, and, I believe, a pretty general one. There was

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also a similar error of something more than one quarter of a degree in laying down the freezing point so that the fundamental interval between freezing and boiling, when the barometer stands at 29,8 inches (the mean height at London) was  $180^{\circ},71$  instead of  $180^{\circ}$ ; by this means each division was in fact  $\frac{1}{260}$ th part less than a degree: this small correction may therefore easily be applied, if thought necessary, but I have taken no notice of it.

I will now add a general table for the use of artists in making this instrument, both according to my own observations, and those of Mr. DE LUC, that the preference may be given as it shall be thought due; not that it is a matter of any great consequence which is made use of under small variations of the atmosphere; but even under these circumstances, I flatter myself, that the object of this paper will be sufficiently obvious to all who wish to verify a new theory, or aim at accuracy in these days of precision.

**Height**

| Height<br>of the<br>barom. | Correct.<br>of the<br>boiling<br>point: | Diff. | Correct.<br>according<br>to Mr. DE<br>LUC. | Diff. |
|----------------------------|-----------------------------------------|-------|--------------------------------------------|-------|
| 26,0                       | -7,09                                   |       | -6,83                                      |       |
| 26,5                       | -6,18                                   | ,91   | -5,93                                      | ,90   |
| 27,0                       | -5,27                                   | ,91   | -5,04                                      | ,89   |
| 27,5                       | -4,37                                   | ,90   | -4,16                                      | ,88   |
| 28,0                       | -3,48                                   | ,89   | -3,31                                      | ,87   |
| 28,5                       | -2,59                                   | ,89   | -2,45                                      | ,86   |
| 29,0                       | -1,72                                   | ,87   | -1,62                                      | ,83   |
| 29,5                       | -0,85                                   | ,87   | -0,80                                      | ,82   |
| 30,0                       | 0,00                                    | ,85   | -0,00                                      | ,80   |
| 30,5                       | +0,85                                   | ,85   | +0,79                                      | ,79   |
| 31,0                       | +1,69                                   | ,84   | +1,57                                      | ,78   |

